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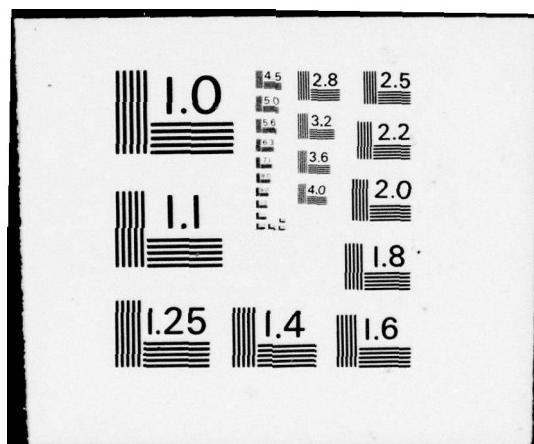
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Technical Report No. 5

THE EFFECT OF THE ENVIRONMENT ON THE MECHANICAL  
BEHAVIOR OF SEMI-CRYSTALLINE POLYMERS  
AT HIGH PRESSURES

by

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exposed to the silicon oil and sealed from it coincide in this region. Silicon oil does however affect both the mechanism and extent of plastic deformation occurring in these polymers. Thus samples of polyethylene and polypropylene which are exposed to the oil show a transition in the mode of plastic deformation from neck formation and propagation at test pressures below 1 to 2 kbar to enhanced ductility without strain hardening. Similar behavior is observed in polyoxymethylene but is less pronounced. In terms of morphology this affect is suggested as possibly occurring due to lamellar slip facilitated by silicon oil plasticized inter-lamellar regions and further experiments are being undertaken to verify this.

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## ABSTRACT

The effect of a silicon oil environment on the mechanical behavior of the semicrystalline polymers polyethylene, polypropylene and polyoxymethylene, under conditions of superposed hydrostatic pressure have been studied. These studies show that silicon oil does not affect the modulus and yield stress of these polymers: thus the modulus and yield stress increase with pressure but stress-strain curves of samples exposed to the silicon oil and sealed from it coincide in this region. Silicon oil does however affect both the mechanism and extent of plastic deformation occurring in these polymers. Thus samples of polyethylene and polypropylene which are exposed to the oil show a transition in the mode of plastic deformation from neck formation and propagation at test pressures below 1 to 2 kbar to enhanced ductility without strain hardening. Similar behavior is observed in polyoxymethylene but is less pronounced. In terms of morphology this affect is suggested as possibly occurring due to lamellar slip facilitated by silicon oil plasticized inter-lamellar regions and further experiments are being undertaken to verify this.

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## INTRODUCTION

The mechanical behavior of the crystalline polymers, polyethylene polypropylene and polyoxymethylene have been studied extensively in recent years (1). The application of hydrostatic pressure causes an increase in both modulus and yield stress of these polymers though there is considerable variance of its effect on their ductility; thus both low and high density polyethylene (2,3,4,5,6) and polypropylene (4,7) show reduced ductility with increasing pressure whereas polyoxymethylene (6,8) shows increased ductility with pressure.

The matter of the effect of the environment (which is the pressure transmitting fluid in such studies) on the mechanical behavior has received little attention except for the observation by Harris, Ward and Parry (9) that polyethylene samples did not seem to be affected by the pressure transmitting fluid (a 50:50 mixture of castor oil and brake fluid) and the study by Davis and Pampillo (10) who reported that polyethylene samples tested in n-pentane exhibited reduced yield stresses relative to those tested in water.

In view of the results of recent studies on the effect of the environment on the mechanical behavior of amorphous polymers (11,12,13) conducted in this laboratory, which show that even seemingly inert environments, e.g. silicon oil used as the pressure transmitting fluid in such studies, cause the polymer to fail in a brittle fashion at pressures at which it is normally ductile, it is highly significant to re-examine

previous results on the effect of hydrostatic pressure on the mechanical behavior of crystalline polymers in terms of the role of the environmental fluid.

This paper presents results on the mechanical behavior of polyethylene, polypropylene and polyoxymethylene, both in the presence of silicon oil, which was used as the pressure transmitting fluid, and in samples which have been 'sealed' from it. The results show that silicon oil, in all three polymers, reduces the amount of plastic deformation prior to failure by inducing brittle-like failure.

## EXPERIMENTAL

Polyethylene, polypropylene and polyoxymethylene samples were obtained commercially as extruded rods 7/8 inches in diameter. Their densities as measured in a density gradient column at 23°C were 0.956, 0.895 and 1.425 g/cm<sup>3</sup> respectively.

Samples for tensile testing were machined directly from the rods and were of the standard round bar type with threaded ends and were of an overall length of 5cm, gauge length of 1.8cm, and diameter of 0.4cm. After machining the samples were carefully polished using fine grade sandpaper followed by soft paper and cotton wool to minimize surface roughness effects. Samples for sealed studies were carbon coated and then covered with silicon rubber (RTV 180 from GE) which was cured for one day at room temperature.

The high pressure apparatus used is a tensile testing machine contained in a pressure chamber filled with silicon oil (Dow Corning 200; viscosity 500 cs) which acts as the pressure transmitting fluid and in unsealed samples is the environment. The apparatus is suitably equipped for photographing the specimen during testing. Applied stress versus strain curves were obtained by pressurizing the sample to the desired pressure followed by straining the sample at a uniform rate while keeping the pressure constant.

The strain-rate was maintained at  $4+0.2\%$  per minute and the specimens were tested at 1 atm, 0.5kb, 1kb, 2kb, 3kb and 4kb pressure at a temperature of  $23+2^{\circ}\text{C}$ . The samples were photographed during the straining process at increments of 1% strain in the case of polyoxymethylene and 2% in the case of polyethylene and polypropylene. The cross-section areas determined from these photographs were used to determine true stress-strain curves.

## RESULTS AND DISCUSSION

1. Polyethylene: The stress-strain curves for polyethylene which is exposed to the silicon oil (unsealed), as a function of hydrostatic pressure, are shown in Figure 1. The results are similar to those for medium density polyethylene obtained by Mears, Pae and Sauer (4) and low density polyethylene obtained by Silano, Bhateja and Pae (6). Modulus and yield stress are both observed to increase with increasing hydrostatic pressure. Plastic deformation on the other hand goes from yield followed by the formation of a stable neck which propagates upto a strain of about 500% before failure, at atmospheric pressure, to yielding followed by neck formation and propagation, but with a decrease in the strain at failure as the pressure is increased between 1 kbar and 2 kbar; the failure surface upto this pressure shows the characteristics of brittle failure in that there is no significant reduction in cross-section of the neck. Thus the process of plastic deformation upto 1-2 kbar can be considered as one of strain hardening (cold drawing with associated orientation). As the pressure is increased above 2 kbar however, yield is followed not by the formation of a stable neck but by a reduction in the cross-section until the diameter reduces to a fine point, i.e. no strain hardening occurs above 2 kbar and the sample attains a state of infinite ductility (as measured by the area reduction ratio).

Figure (2) shows the stress-strain behavior of sealed polyethylene samples. As in the case of the polyethylene samples which are exposed to the silicon oil environment the modulus and yield stress are observed to increase with increasing hydrostatic pressure; however, unlike the unsealed samples there is no large decrease in the amount of plastic deformation prior to failure with increasing hydrostatic pressure and the formation of a stable neck which propagates is observed right upto the largest pressure of test i.e. 4 kbar.

That the stress-strain behavior of sealed and unsealed samples is identical except in terms of the mechanism and extent of plastic deformation can be further seen from Figure 3, which shows superposition of their true stress-strain curves upto the point where the diameter of the neck begins to reduce in the unsealed samples. The difference in the nature and magnitude of plastic deformation in sealed and unsealed samples is clearly depicted in photographs of these samples taken subsequent to their having been tested at various pressures, Figure 4.

2. Polypropylene: The stress-strain data for unsealed polypropylene samples as a function of hydrostatic pressure are similar to those obtained by Pae, Mears and Sauer (4,7) and are shown in Figure 5. As in the case of polyethylene the modulus and yield stress increase with pressure, the amount of plastic

deformation prior to failure decreasing. The stress-strain behavior of sealed polypropylene samples, Figure 6, shows, as observed in the case of sealed polyethylene samples, that the sealing acts to suppress plastic deformation at higher pressures. The true-stress-strain curves for sealed and unsealed samples superpose upto the point of 'crack initiation' in the necked region of unsealed samples, Figure 7. As in polyethylene, examination of the tested samples (unsealed) Figure 8 shows a transition in behavior from neck formation and propagation followed by brittle-like failure at pressures below 2 kbar to suppression of cold drawing with an associated enhancement of ductility above it. In this respect our results differ from those of Mears, Pae and Sauer (4) who observed a crack to form even at pressures upto 7 kb. In the case of sealed samples, Figure 8, the polymer deforms by neck formation and propagation with more than one neck being observed at higher pressures. It was not possible to strain these samples to failure because of limitations of cross-head travel in the high pressure cell.

Thus, as in the case of polyethylene the silicon oil environment induces a transition from cold drawing to ductile behavior at a pressure between 1 kb and 2 kb, thereby reducing the amount of plastic deformation, without in any way affecting either the modulus or yield stress.

3. Polyoxymethylene: The stress-strain behavior of unsealed polyoxymethylene samples as a function of pressure is shown in

Figure 9 and is in agreement with the results of Sardar, Radcliffe and Baer (8) and Silano, Bhateja and Pae (5). As in the case of polyethylene and polypropylene the modulus increases with increasing hydrostatic pressure. At atmospheric pressure the samples deform homogeneously and fracture occurs before the attainment of yield i.e. in a brittle fashion. As the hydrostatic pressure is increased to 1 kbar yielding occurs but no macroscopic necking can be observed as can be seen in photographs of unsealed after being tested at pressures upto 1 kbar, Figure 12. As the pressure is increased above 1 kb necking is observed and its contribution to deformation increases with increasing pressure. Contrary to the observation in polyethylene and polypropylene the strain at failure increases with pressure in the case of unsealed polyoxymethylene samples.

Figure 10 shows the stress-strain behavior of sealed polyoxymethylene samples as a function of hydrostatic pressure. As in the case of polyethylene and polypropylene sealing increases the amount of plastic deformation that can occur before the sample fails. Sealing also changes the nature of deformation in that necking is observed at pressures of 0.5 kbar and 1 kbar at which pressure the unsealed sample shows macroscopic brittle failure characteristics. At higher test pressures there is neck formation and propagation but since the strains at which failure occurs are small, compared to polyethylene and polypropylene, this is not visually as obvious.

As in the case of polyethylene and polypropylene superposition of the true-stress strain curves of sealed and

unsealed samples is observed, Figure 12, upto the point of plastic deformation indicating that the role of the silicon oil is restricted to suppressing cold drawing and inducing ductility.

### CONCLUSIONS

Studies on the effect of a silicon oil environment on the mechanical behavior of the semi-crystalline polymers polyethylene, polypropylene and polyoxymethylene as a function of hydrostatic pressure show that there is no measurable effect of the oil on the modulus and yield stress of the polymer i.e. the modulus and yield stress are observed to increase with hydrostatic pressure identically for sealed and unsealed samples. The amount of plastic deformation prior to failure is however substantially effected by the silicon oil. In the case of polyethylene and polypropylene, sealed samples exhibited the formation of a neck which propagates at a constant stress over the entire pressure range studied i.e. upto 4 kbar. Failure occurs by the brittle like failure of the cold drawn polymer and is not accompanied by a large reduction of the diameter of the propagating neck. Samples which are exposed to the silicon oil environment, however, show a transition from plastic deformation by neck formation and propagation to one of enhanced ductility as manifested by a gradual and continuous reduction of the sample cross-section, as the pressure of testing is increased above 2 kbar; the silicon oil thus appears to be plasticizing the polymer such that plastic deformation can occur without strain hardening or orientation.

In terms of morphology the action of silicon oil at high pressure may be considered as occurring due to strain enhanced diffusion into inter-lamellar regions which are

plasticized by the silicon oil such that lamellar slip can occur at a lower stress than is required to cold draw and orient the sample (14) thus giving rise to enhanced ductility. Experiments to examine orientation in the region of samples which show these failure characteristics are being undertaken.

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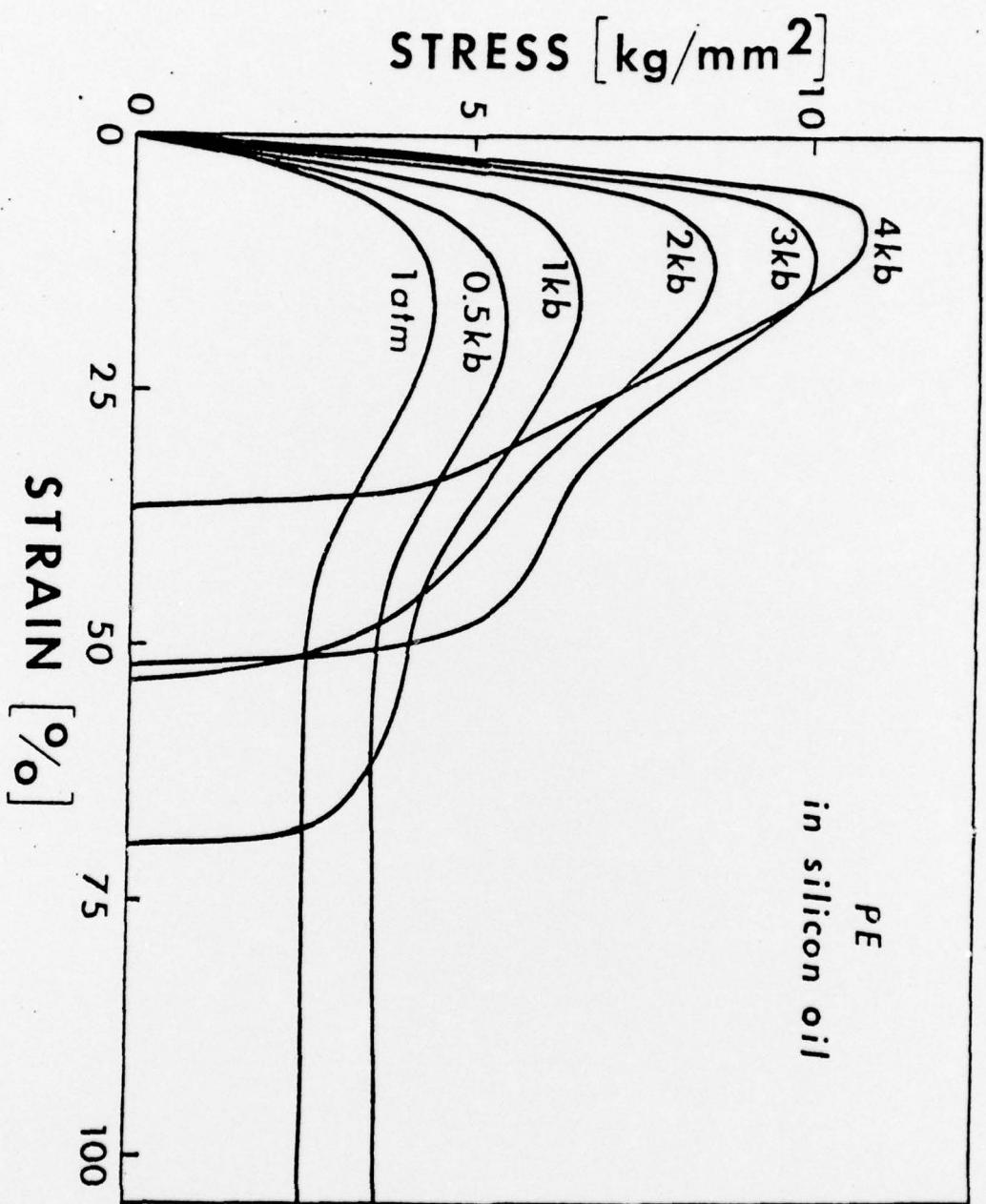


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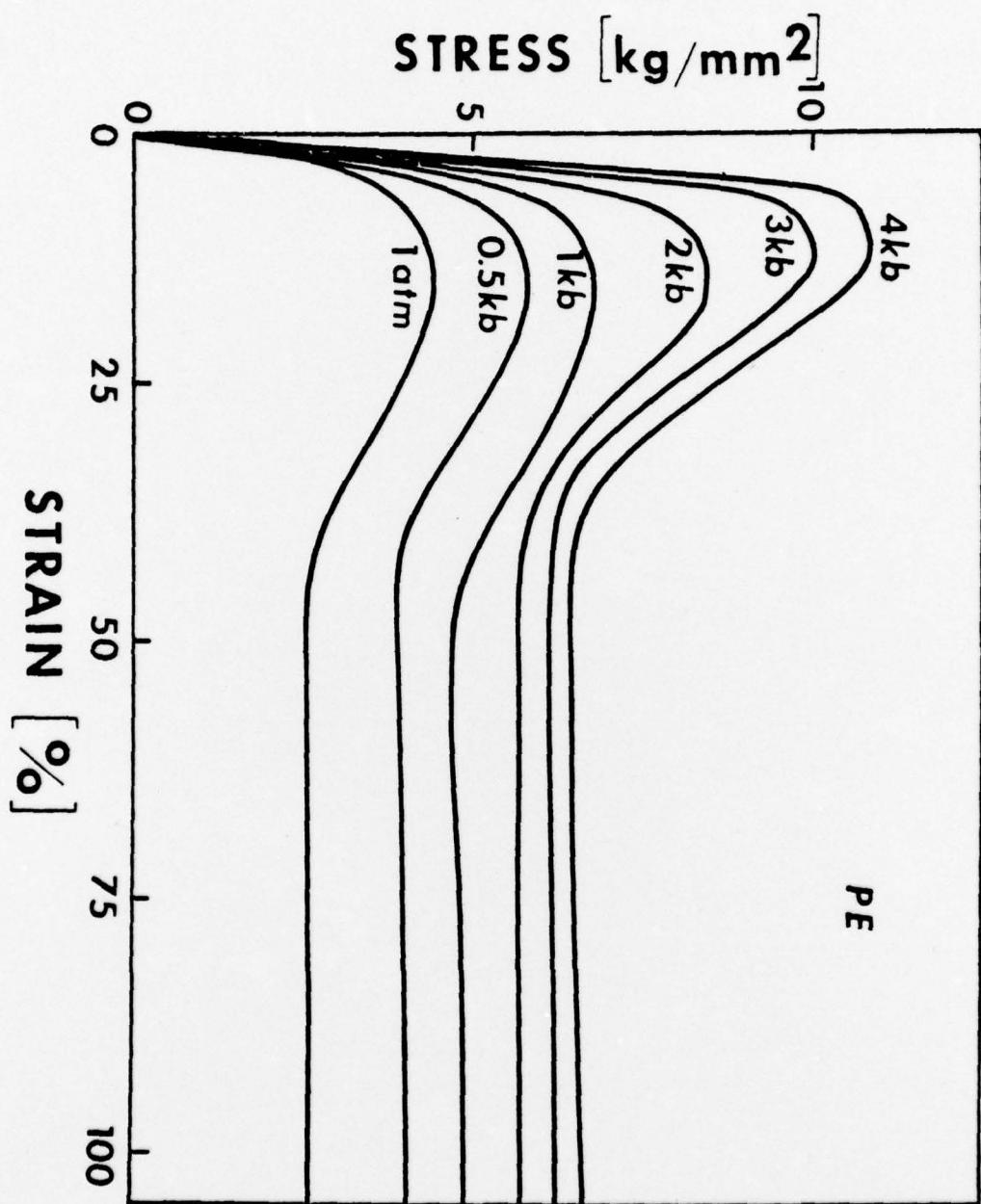


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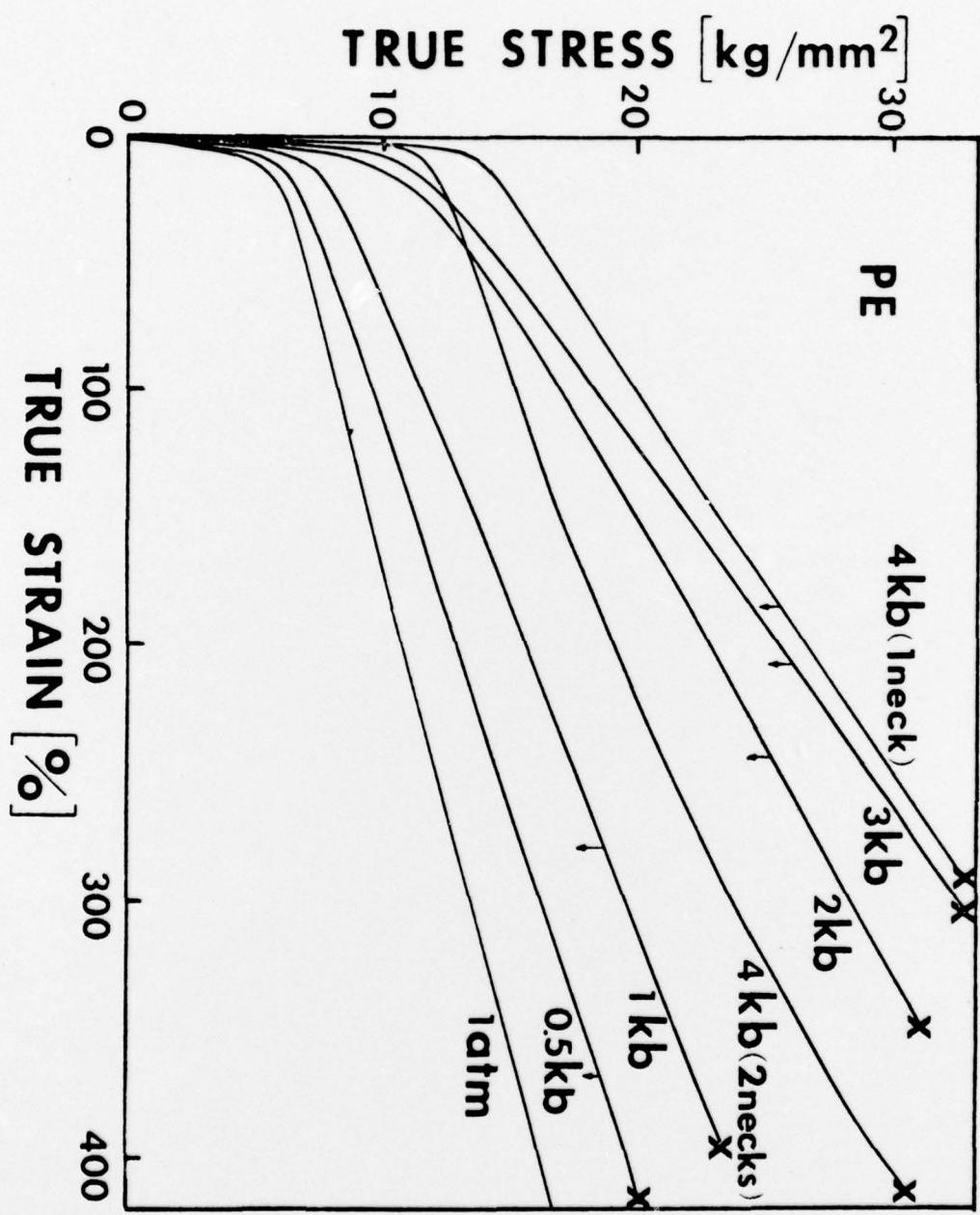


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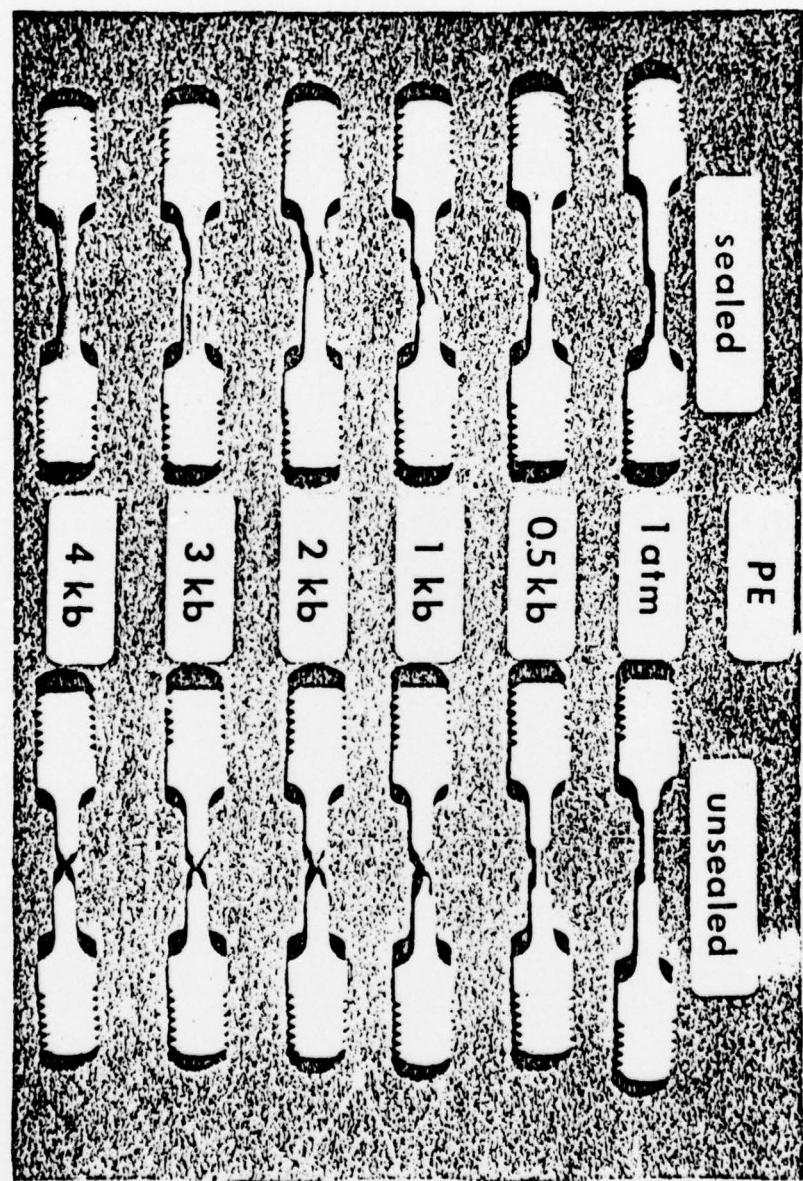


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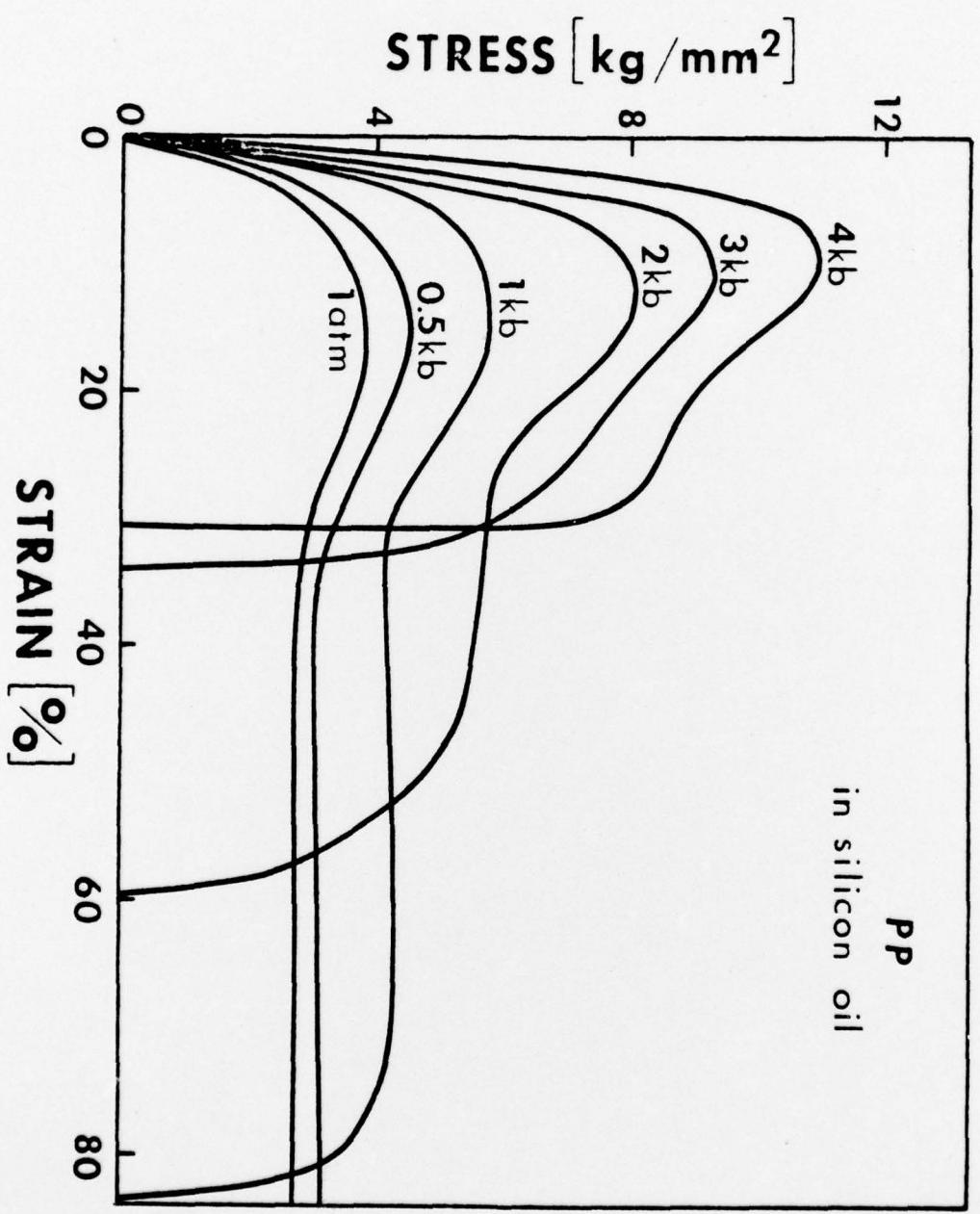


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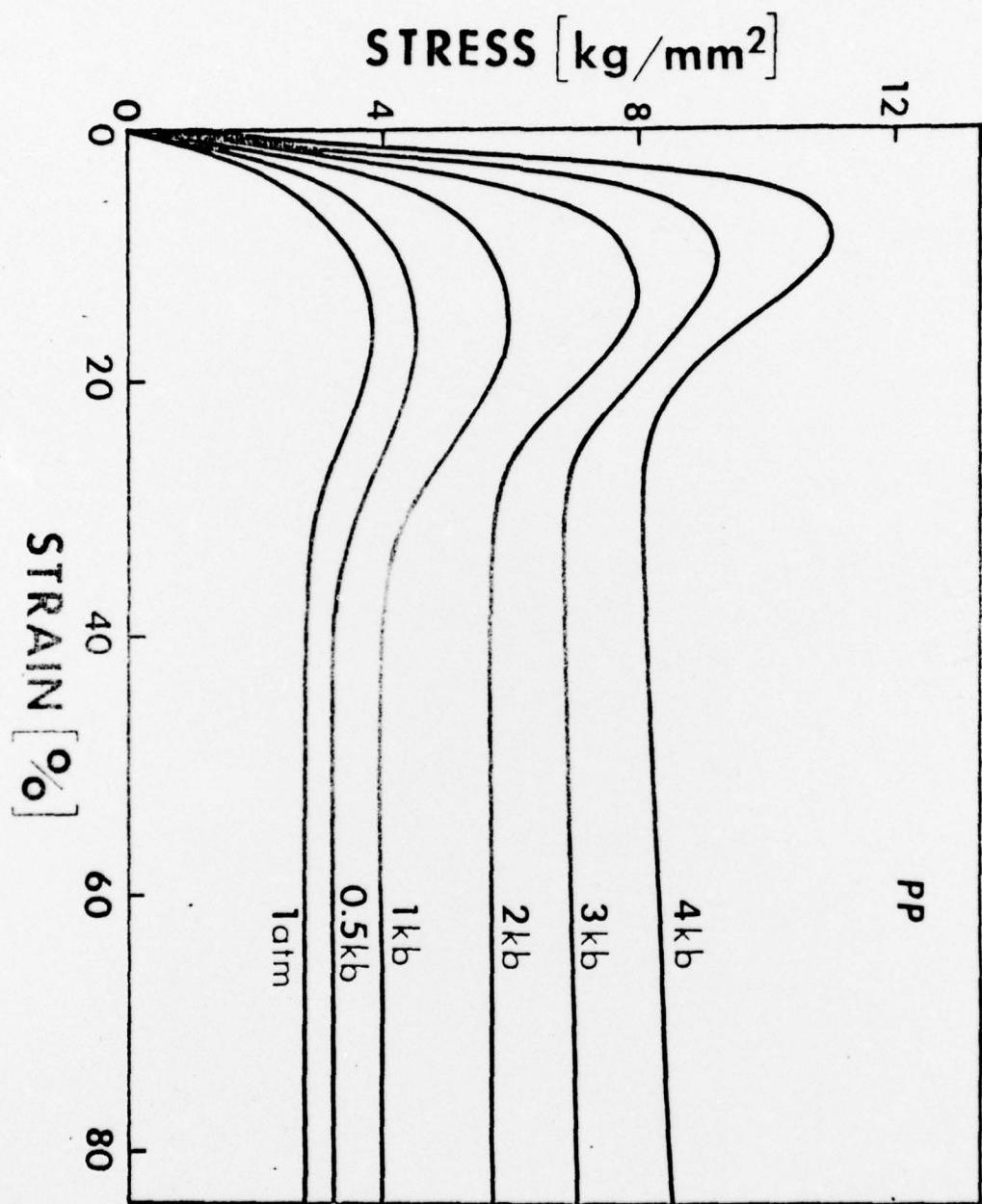


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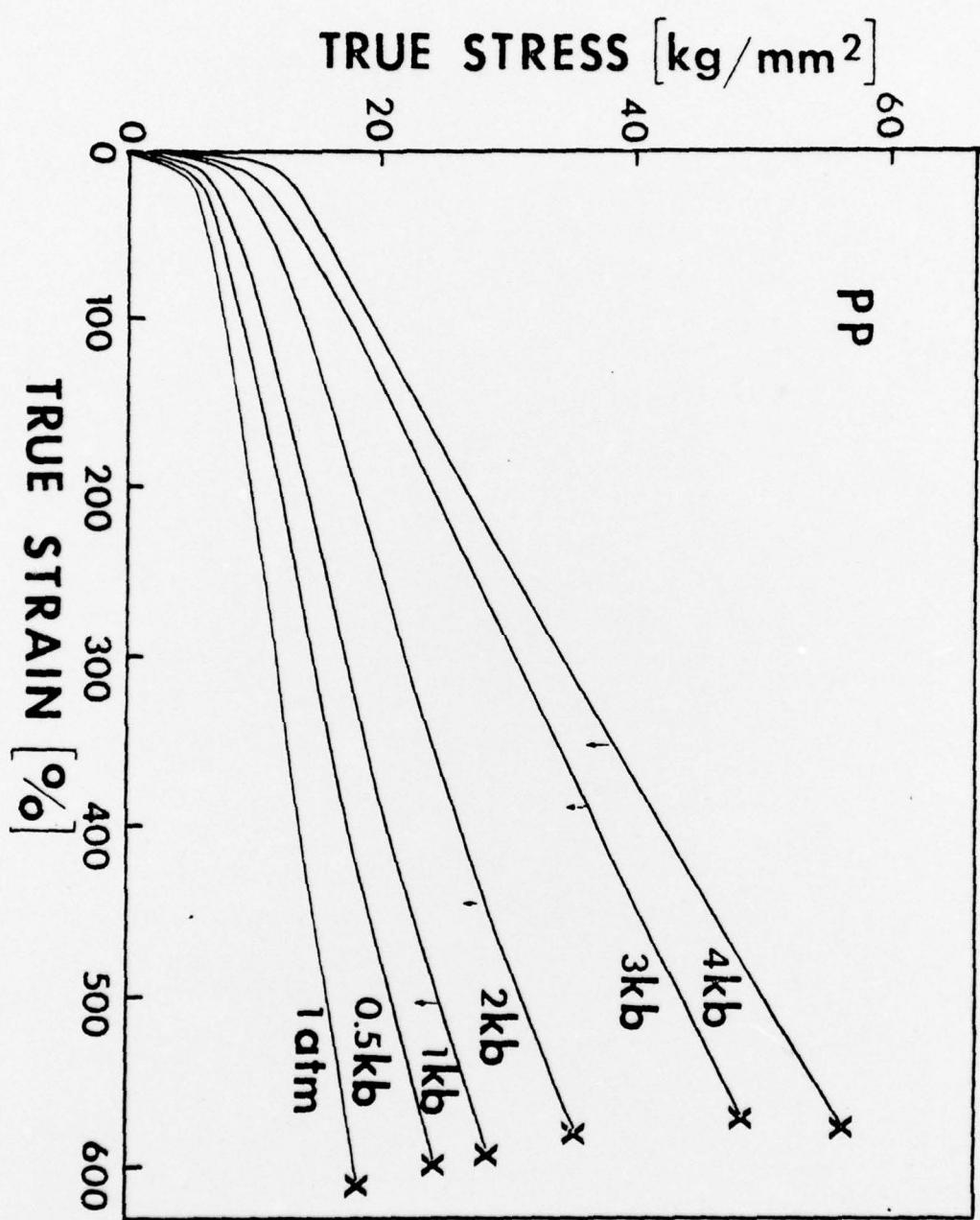


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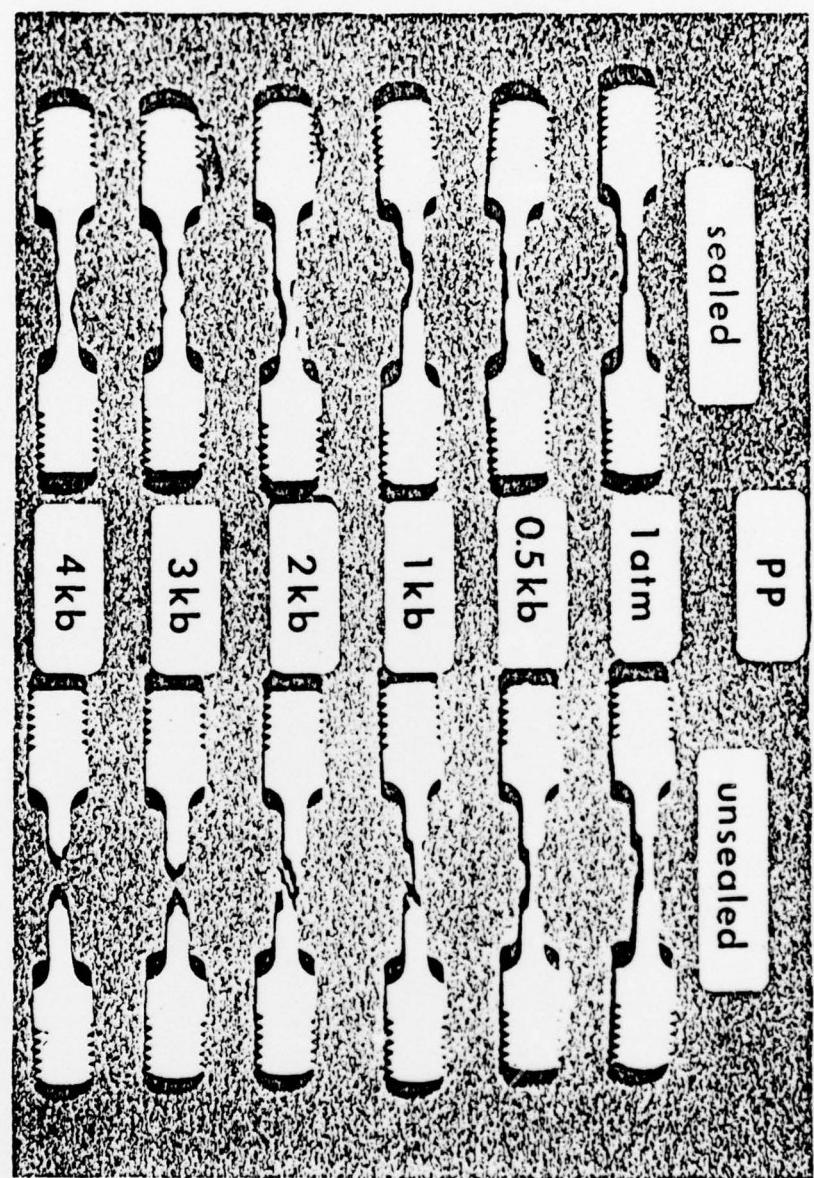


Figure 8

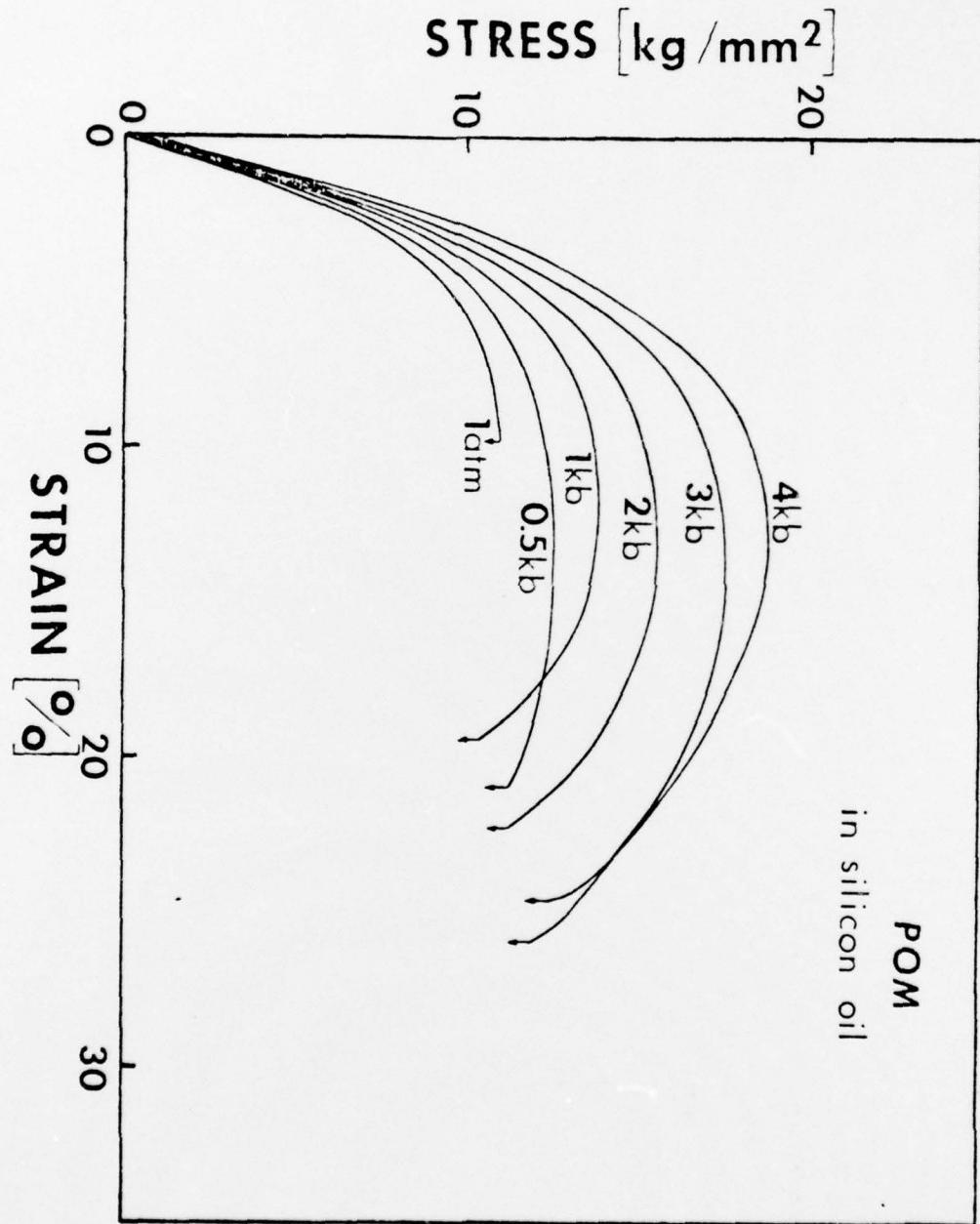


Figure 9

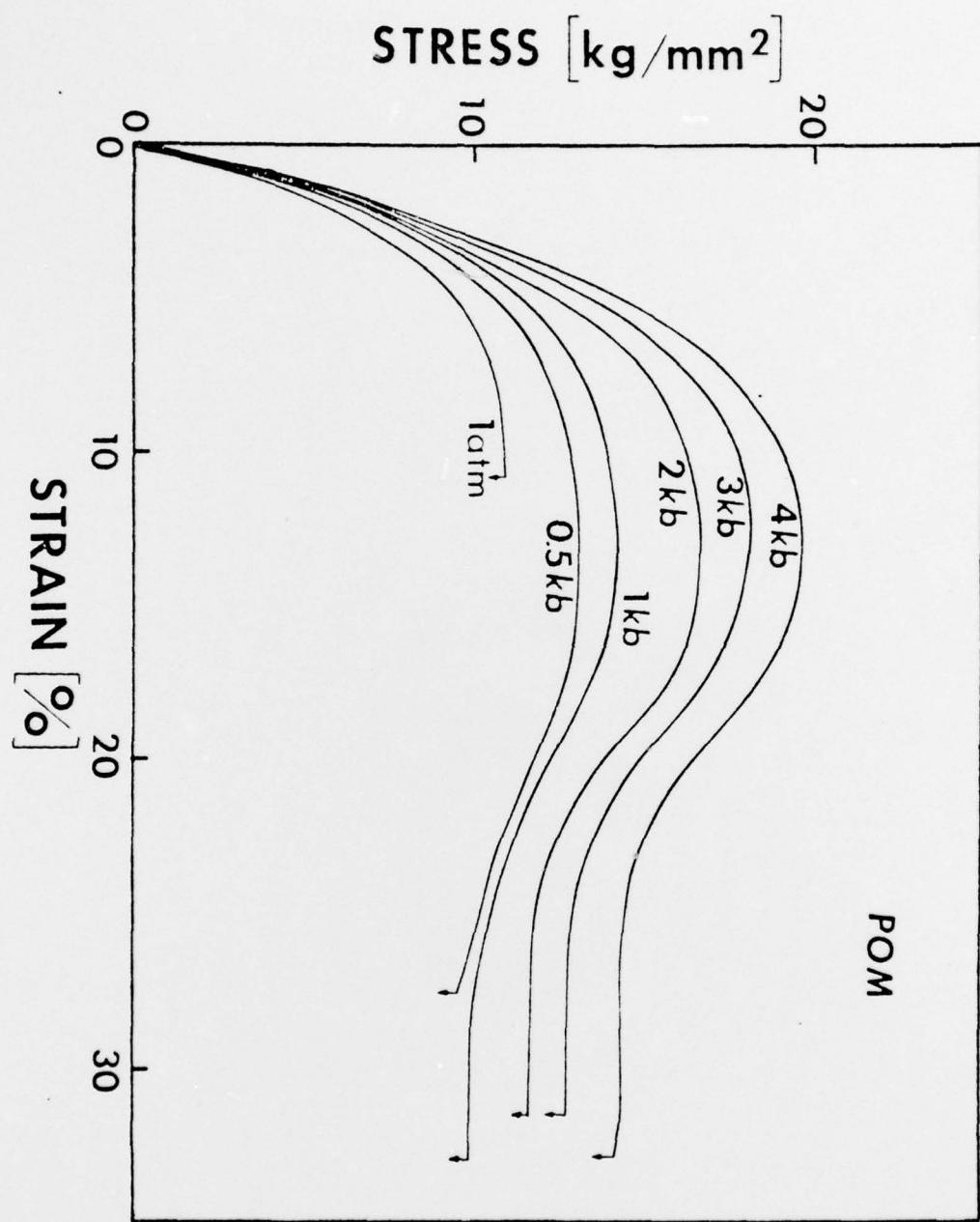


Figure 10

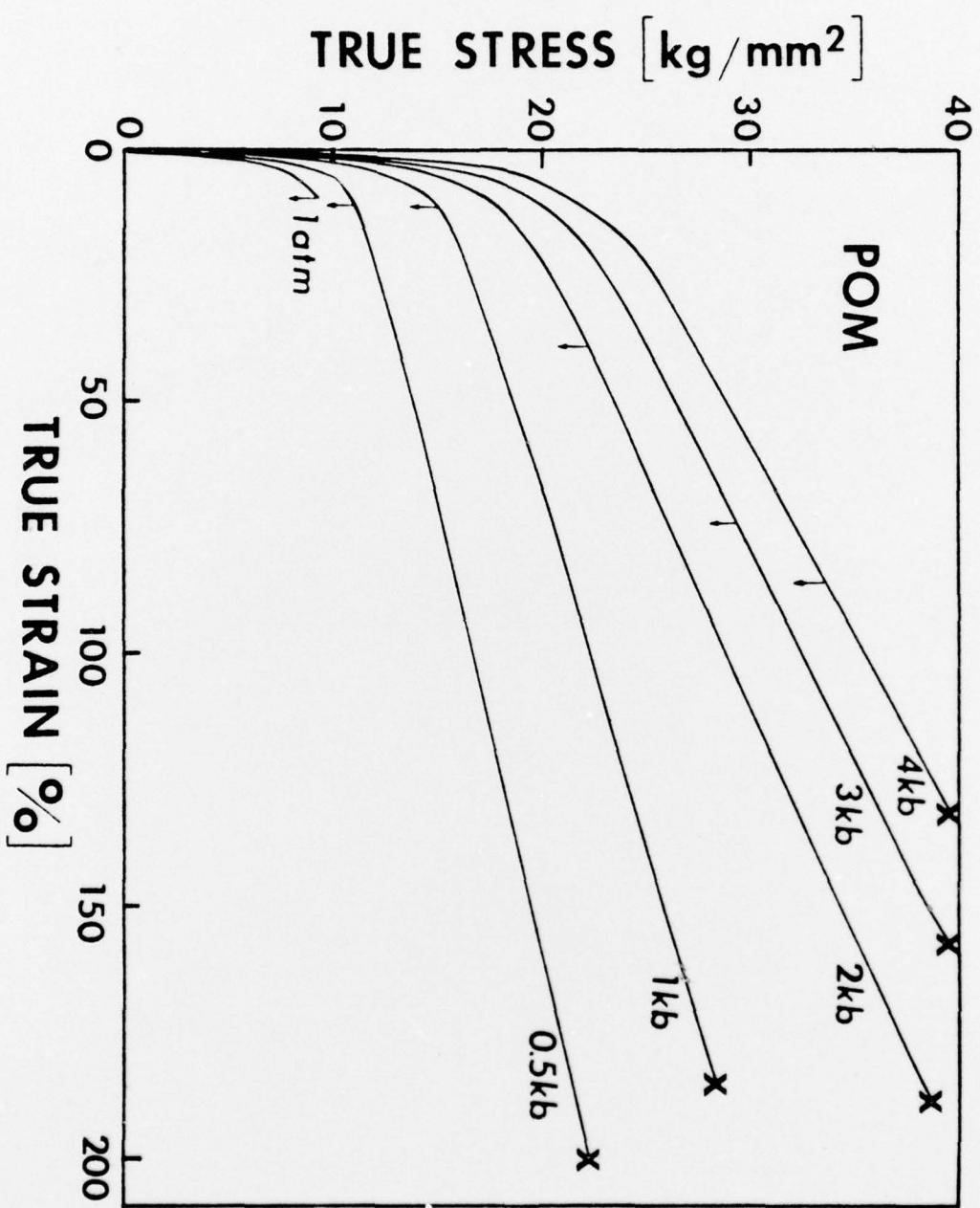


Figure 11

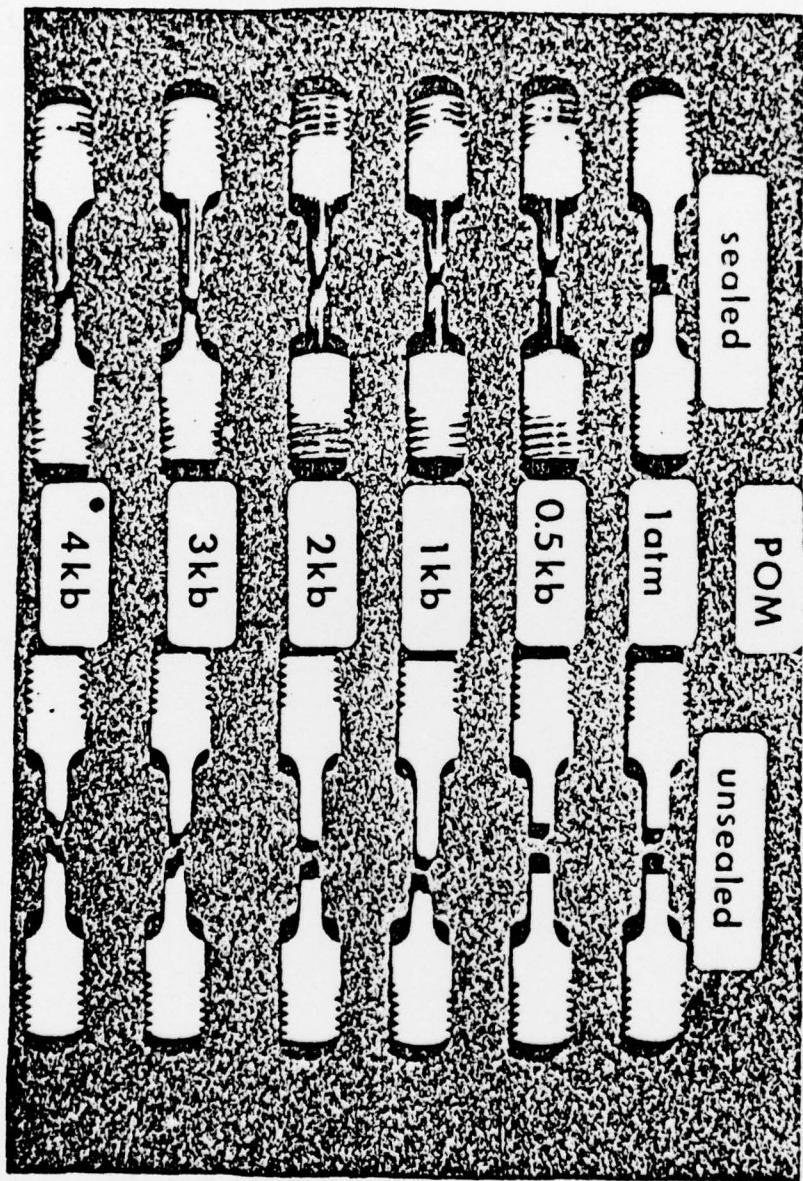


Figure 12